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ELECTROCHEMICAL PREPARATION OF POLYMER ELECTRODES(U)
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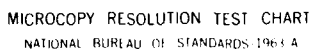
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Polymer electrolytes formed by the chemical and electrochemical polymerization of a solution of LiAsF_6 in dioxolane have been examined. The liquid electrolyte has been stabilized by preparing and storing it in the presence of Li metal as a proton and carbocation scavenger. The initial results show that the polymerization of the electrolyte is readily initiated chemically by acids or oxidizing agents. The polymerization continues so that over 24 hrs at room temperature the conductivity of the resulting polymer electrolyte decreases to near 10^{-6} S/cm. These results are to be reported in a paper submitted to the Journal of the Electrochemical Society (Technical Report #1). Subsequent work involved the preparation of free standing films and TiS_2 electrodes containing the polymer electrolyte. Lithium/ TiS_2 cells were constructed and evaluated at room temperature and 60°C .

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INTRODUCTION

See the attached publication (Technical Report #1) entitled "Polydioxolane Polymer Electrolyte" which has been submitted for publication in the Journal of the Electrochemical Society.

ADDITIONAL RESULTS AND DISCUSSION

TiS₂ Electrodes Incorporating the LiAsF₆ Polymer Electrolyte (PE) in Lithium Cell. A potential use of the EC formation of a polymer electrolyte is to form the electrolyte in situ in a cell. This would be done by anodically polarizing the positive electrode (e.g., TiS₂) to initiate the formation of polymer. It was also suggested that a PE so formed would provide excellent interfacial contact with electrode material. Thus the formation of the polydioxolane PE in TiS₂ electrodes was investigated and the resulting electrodes were incorporated into Li cells.

Two types of cells were used to electrochemically form the PE. One cell was essentially a Li/TiS₂ cell. The liquid dioxolane/LiAsF₆ electrolyte was added to the cell and the cell voltage driven to overcharge, i.e., the TiS₂ electrode was driven to potentials sufficiently anodic to initiate polymerization (greater than ~3.2V vs. Li). Such a cell was made, the polymerization initiated, and the cell was allowed to set for more than 24 hrs to complete polymerization. On discharge at room temperature, the cell maintained a discharge rate of 0.020 mA/cm² with an iR drop of 0.6V.

Assuming an electrolyte thickness of ~0.01 cm (1 mil Celgard plus an average additional gap due to surface irregularities), the effective conductivity during discharge is ~10⁻⁷ S/cm. This conductivity is less than would be expected from earlier work by an order of magnitude. This could be explained by the presence of the Celgard separator, or due to continuing polymerization (or crystallization), to ion concentration polarization, and/or to interfacial effects. In another cell, the TiS₂ electrode could not be driven to a potential great enough to form the polymer. This may have been due to a partial short across the cell or to soluble reduced materials which were preferentially oxidized at the TiS₂ electrode.

Subsequently a second type of cell was used to form the PE in TiS₂ electrodes. This cell consisted of a TiS₂ electrode sandwiched between two stainless steel electrodes. It was hoped that this cell would allow the formation of cathodes containing the PE in a more reproducible manner. The initiation was done galvanostatically with the potential of the TiS₂ electrode being allowed to rise to greater than 3.5V. In later experiments the voltage was monitored and allowed to rise to 7.0V. In these experiments an



inflection in the voltage profile was noted at ~3.5V with a subsequent rise to 7.0V due mostly to the increased resistance across the cell. Hopefully, uniform voltage profiles would be obtained with the appearance of the voltage profile being characteristic of a particular liquid electrolyte/PE interconversion. Unfortunately considerable variation was observed with the variable nature of individual TiS_2 electrodes probably making a contribution.

Nonetheless, TiS_2 electrodes were prepared in this manner. After the initiation of polymerization, the cell was allowed to set for typically one hour and the excess liquid electrolyte surrounding the cell package was removed. After an additional wait of more than 24 hrs, the cell was disassembled and the TiS_2 electrode (contained in a Celgard bag) removed. This was then placed between Li electrodes to form a cell which was placed under light pressure. Unfortunately the cells so constructed using cathodes which appeared to incorporate fully polymerized PE, gave low discharge rates again corresponding to PE conductivities of $\sim 10^{-7}$ S/cm. Cathodes which contained PE less fully polymerized (sticky, soft) gave cells that could maintain higher discharge rates.

A cell similar in construction to those above was discharged at 60°C. As expected, this cell could be discharged at a much higher rate due to the increased conductivity of the electrolyte.

In the above cells, the accessible rates were very low at room temperature perhaps partially due to the presence of the Celgard separator necessary to keep the electrodes from shorting prior to polymerization. Fabricating cells without a Celgard separator proved difficult. If the PE was formed in the TiS_2 while suspended in bulk electrolyte, then the films on the surface tended to become thick giving a highly resistive cell. Attempts to make thin films gave shorts in the assembled cells. A grossly porous separator might be used but with TiS_2 individual grains of the cathode material tended to short through the separator. A major problem in growing surface films of PE was that the initiation conditions appear to be very sensitive to the history of the particular cathode used and the purity of the particular batch of electrolyte used.

Free Standing Films. Attempts were also made to form free standing films by EC initiation. These might be used as separators in cells or in studies of the properties of the polydioxolane PE. The approach was to confine a thin layer of liquid electrolyte in a cell with electrodes separated only by a narrow gap. Such a cell was used to prepare thin films and allow the measurement of their conductivities in the work reported in the attached paper. Unfortunately the films formed in this cell adhered very tightly to the anode and thus it was very difficult to remove the film without significantly damaging it.

Another approach to making free standing films is to first form the polymer and then add the electrolytic salt. The film would then be formed from solution as is typically done in forming other polymer electrolytes. Samples of high molecular weight polydioxolane were synthesized, however there was insufficient time to pursue this line of research.

Polydioxolane Containing Other Electrolytes. Two other electrolytic salts were investigated for use with dioxolane in forming EC initiated polymer electrolytes. These salts were LiBF_4 and LiSO_2CF_3 . The liquid electrolytes prepared using these salts (2.5 m) were much less conductive than the LiAsF_6 electrolyte, both $\sim 0.001 \text{ S/cm}$, and the fluoroborate electrolyte polymerized on standing. A more dilute fluoroborate solution was prepared (1.0 m). It and the trifluoromethane sulfonate solution were EC polymerized in a TiS_2 electrode and a Li cell assembled. Both of the cells had much higher internal resistance than previously observed using LiAsF_6 .

Summary. Although it appears that a polydioxolane PE can successfully be formed by means of EC initiated polymerization, the polymerization is difficult to control and the properties of the PE are variable. The conductivity of this PE is similar to the more conductive of the polyethylene and propylene oxide PE's especially in cases in which relatively complete polymerization of the polydioxolane takes place. The Li/ TiS_2 cells constructed using the polydioxolane PE operated only at very low rates at room temperature.

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